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Thesis

REACTIONS OF 2-NITROBUTENE-1

by

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TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

- 0 -

I. INTRODUCTION

A. General

With the vapor-phase nitration of hydrocarbons, first employed by Hass, Hodge, and Vanderbilt (24, 25, 26) at Purdue University, an abundant supply of nitroparaffins has been made possible. As a result of the commercial production of several nitroparaffins research has been greatly stimulated in the field of nitro compounds. For example, a large number of nitroalcohols has been prepared by condensing nitroparaffins with aldehydes. These alcohols have been converted to the corresponding nitroölefines by various methods.

Although several references have been found concerning the tendency of nitroölefines to polymerize, no detailed study has been reported. In the course of this work several compounds have been tested as catalysts for this polymerization. Among these compounds were various amines. Since there is a possibility that some of the amines may also undergo a 1,4-addition to the nitroölefines, these two types of reactions have been studied.

B. Survey of Literature on Preparation of Nitroölefines

1. From Olefines

Nitroölefines have been prepared in low yields by the nitration of olefines with the anhydride of nitric acid (nitrous fumes) at 0°C. The action of nitrous fumes on trimethylethylene produced 2-methyl-3-nitrobutene-2 (38). Wieland (59) carried out the same reaction using concentrated nitric acid. Diamines have been obtained generally in low yields by reduction of the crude, and of the purified, solid products formed by the action of nitrous fumes upon ethylene (12), propylene (13), butene-1 (14), and isobutylene (50). It was assumed that a considerable portion of the product on nitration was the unsaturated nitro compound.

x-Nitroöctylene was reported to have been prepared by the direct nitration of octylene with moderately concentrated nitric acid (31).

xx-Dinitroöctylene has been prepared by treating octylene first with dilute nitric acid and then with nitrosulfuric acid (39).

Diphenylbutadiene has been shown to react with nitrogen dioxide to produce 1,4-diphenyldinitrobutene-2 (60). The action of alkalis on this compound produced the mononitrocompound 1,4-diphenyl-1-nitrobutene.

Styrene plus nitric acid gave nitrostyrene. This reaction resembles that of nitric acid with isobutylene (56).

Wieland and Stenzl (60) prepared 1,4-dinitro-1,4-diphenyl-

butene from diphenylbutadiene and nitrogen dioxide.

2. From Unsaturated Alkyl Halides

Askenasy and Meyer (3) reported the preparation of 3-nitropropene-1 by heating silver nitrite and allyl iodide in sand. Henry (29) reported the same compound using allyl bromide and silver nitrite.

$$CH_2{=}CHCH_2Br + AgNO_2 \longrightarrow CH_2{=}CHCH_2NO_2 + AgBr^1$$

The reaction of alcoholic potassium nitroethane and allyl iodide yielded 4-nitropentene-1 (17).

3. From Tertiary Alcohols

Haitinger (19) has prepared 1-nitro-2-methylpropene from trimethyl carbinol and concentrated nitric acid.

$$(CH_3)_3COH + HNO_3 \longrightarrow (CH_3)_2C{=}CHNO_2 + 2HOH$$

Haitinger (20) also reported the formation of 3-nitro-2-methylbutene-2 from dimethylethylcarbinol. On heating the latter with water at 100°C., nitroethane and acetone were formed.

Small yields of 1-nitro-2-methylpropene-1 along with carbon monoxide and acetone have been obtained from sebacic acid and concentrated nitric acid (21).

4. From Nitroalcohols by Dehydration

Several syntheses of nitroölefines by the dehydration of

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[1] Brackenbush (8) first reported this reaction but his work was attacked and discredited by Schiff (44) who showed that he had not prepared a new nitroölefine but in reality the substance he reported as boiling at 96°C. was mostly water.

nitroalcohols have been reported. Bouveault and Wahl (7) prepared 1-nitrohexanol-2 by condensation of valeraldehyde and nitromethane and dehydrated the nitroalcohol with anhydrous zinc chloride in glacial acetic acid solution to form 1-nitrohexene-1.

A similar preparation for 5-nitro-2-methylpentene-4 (5, 7) has been recorded.

Cerf de Mauny (10) carried out the same reaction but used acetic anhydride heated to 120°C. as the dehydrating agent. He also prepared 1-nitrotridecylene by this method. Wieland and Sakellarios (57) obtained nitroethylene by the dehydration of 2-nitroethylalcohol with sodium bisulfate. The violent reaction of 2-nitroethyl nitrate and phosphorus pentoxide produced nitroethylene (58). Nitroethylene and 1-chloro-1-nitroethylene (61) have also been prepared by the dehydration of the corresponding alcohols with phosphorus pentoxide.

Organic nitro compounds containing an unsaturated linkage have been obtained by condensing formaldehyde with a nitro compound of the type formula RCH_2NO_2 when R is hydrogen, halogen, or a substituted or unsubstituted alkyl or aryl group. The condensation was effected by bringing the heated reagents in the vapor-phase in contact with a dehydration catalyst. Hasche (22) used this method to prepare the following compounds: nitroethylene, β-nitrostyrene, nitropropylene, nitrobutene. Naphthylnitromethane was also used in this process.

5. From Aldehydes and Nitroparaffins

Alpha and beta unsaturated nitro compounds can be ob-

tained by condensing aromatic aldehydes with aliphatic nitro compounds. The alpha hydrogen of the nitro compound adds to the carbonyl oxygen in an aldol condensation.

$$RCHO + CH_3NO_2 \longrightarrow [RCHOHCH_2NO_2] \longrightarrow RCH{=}CHNO_2 + H_2O$$

Considerable work resulting in the variation of this type of reaction has been recorded. Worrall (66) has published details for the condensation of benzaldehyde and nitromethane by sodium hydroxide to form good yields of β-nitrostyrene. Although Simon (48) had made this compound from styrene long before, the first preparation by this condensation was made by Priebs (41) who used zinc chloride as a catalyst. Posner (40) confirmed and extended this work, but later Thiele (53) reported much better results using alcoholic potassium hydroxide followed by acidification with hydrochloric acid. Sodium hydroxide has been substituted for the potassium analogue. Bouveault and Wahl (6) used sodium methoxide in place of potassium hydroxide.

Thiele (53) found that when the alkali salt was acidified with a mineral acid, nitrostyrene resulted, but when acetic acid was used, the corresponding nitroalcohol was obtained. This result was corroborated by Holleman (30) and also by Rosenmund (43).

Terephthalaldehyde has been condensed with nitromethane, nitroethane, phenylnitromethane, and p-bromophenylnitromethane, using various amines as catalysts, to give the corresponding nitroölefines (65).

Thiele (53, 54) has prepared p-phenylene-bis-nitroethylene

from nitromethane and terephthalaldehyde by condensation in presence of an alkali.

Knoevenagel and Walter (32) obtained good results by adding small amounts of a primary aliphatic amine to a mixture of nitromethane and benzaldehyde.

$$C_6H_5CHO + RNH_2 \longrightarrow C_6H_5CH{=}NR + H_2O$$

$$C_6H_5CH{=}NR + RCH_2NO_2 \longrightarrow RNH_2 + C_6H_5CH{=}C(NO_2)R$$

Worrall (64) modified the Knoevenagel method by showing that aromatic as well as aliphatic primary amines were effective in catalyzing the condensation of aromatic aldehydes with nitromethane to form unsaturated compounds. He proved this by producing nitrostyrene from nitromethane and benzaldehyde, using amyl amines, benzalbutylamine, diethylamine, dibenzylamine, dibutylamine, and diethanolamine as catalysts. With tertiary aliphatic amines only nitroalcohols were formed. Nitrostyrene is easily formed by distilling 1-phenyl-2-nitroethanol with traces of acid (64).

Worrall (65) has also prepared dinitrovinylbenzene, 1,4-bis(β-nitro-β-phenyl-vinyl)benzene and 1,4-[bis β-nitro-β (4-bromophenyl)vinyl] benzene by condensing the aldehydes and the appropriate nitro compounds with various amines as catalysts.

Hydroxy substituted nitroölefines may be produced by condensing unsaturated aldehydes with nitroparaffins (49).

A very convenient table listing the aromatic nitroölefines together with references to the methods of preparing them, has been prepared by Hass and Riley (27).

6. From the Acetates of Nitroalcohols

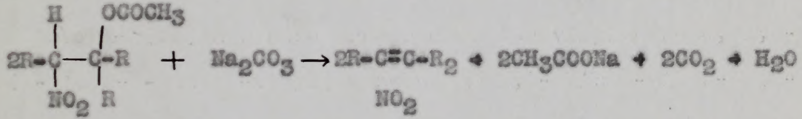
It is known that unsaturated nitro compounds can be obtained by causing aromatic aldehydes such as benzaldehyde to react with nitromethane. On the other hand, the interaction of aliphatic aldehydes or ketones with aliphatic nitroparaffins results in the formation of nitroalcohols.

Schmidt and Rutz (45) have prepared several nitroölefines from the acyl derivatives of the corresponding alcohols, prepared by condensing nitromethane with aldehydes. These esters, when heated for several hours in ether with potassium bicarbonate, decompose with remarkable ease.

$RCH(OR')CH_2NO_2 \longrightarrow RCH{=}CHNO_2 + R'OH$ where $R' =$ acyl.

In this way, 1-nitroöctylene, 1-nitropropene, 1-nitrobutene-1, and 1-nitropentene-1 were prepared.

Susie (51) represents a modification of this reaction by the following equation:



$$2R-\overset{H}{\underset{NO_2}{C}}-\overset{OCOCH_3}{\underset{R}{C}}-R + Na_2CO_3 \rightarrow 2R-\underset{NO_2}{C}{=}C-R_2 + 2CH_3COONa + 2CO_2 + H_2O$$

Schwarz and Nelles (46) have patented a process in which an aliphatic O-acetylated nitroalcohol having at most eight carbon atoms in the alcohol residue of the ester is treated with an alkaline substance, as a salt of a weak acid such as sodium acetate in less than the stoichiometric proportions. This method does not require the use of a solvent. The writers recorded the following compounds prepared by this method:

1-nitropropylene from 1-nitroiospropyl acetate and sodium acetate

1-nitropropylene from β-nitropropylpropionate and potassium carbonate

1-nitropentylene from 1-nitropentanol-2-acetate and sodium hydroxide

1-nitroamylene from 1-nitropentanol-2-acetate and sodium hydroxide

1-nitroöctylene from β-nitroöctylacetate

4-methoxynitroamylene from O-acetyl-1-nitro-4-methoxypentanol and sodium acetate

2-methyl-3-nitropropene-1 from 2-methyl-3-nitro-pentanol-4-acetate and sodium acetate

3-methyl-2-nitrobutene-1 from 3-methyl-2-nitrobutanol-1-acetate and sodium acetate

C. Survey of Literature on Polymerization of Nitroölefines

Although several references have been found concerning the tendency of nitroölefines to polymerize, no detailed study of these polymers or of their formation has been reported.

Wieland (57) has noted that a drop of nitroethylene added to water formed colorless, insoluble flocks of a polymer; with alkalis the polymerization took place violently with evolution of considerable heat. Heating did not decompose the polymer which decomposed with feeble deflagration. It was soluble in alkalis, producing a yellow color.

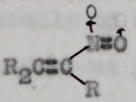
In his work with nitrostyrene, Worrall (63, 62, 63) frequently mentioned the ease of polymerization of nitrostyrene. Worrall (65) also found that β-β-dinitrovinylbenzene forms an amorphous polymer in the presence of ammonia.

In the preparation of nitropropylenes Schmidt (45) reported a considerable reduction in yield because of their tendency to polymerize. Although 1-nitro-1-propylene is quite stable when pure, it shows a great tendency to polymerize, especially in the presence of alkalis, forming a yellow-brown solid polymer which is soluble in sodium hydroxide. With higher homologues the yields are satisfactory. However, it was noted that a decrease in tendency to polymerize with increasing molecular weight was less marked in the nitrochloroölefines than in the nitro series.

In the presence of sodium bicarbonate, 1-chloro-1-nitroethylene was transformed into a solid polymer which decomposed at 126-130°C. (61).

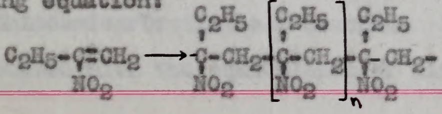
In general, the rate of polymerization increases with increase in unsaturation along a given chain of carbon atoms in a compound. The relative position of the unsaturated linkages along a given chain of carbon atoms in a compound has a large effect upon the rate of polymerization. The most rapid rate is found in compounds having conjugated, unsaturated linkages. Substituents on the unsaturated carbon atoms are capable of influencing the polymerizing tendencies. Prominent among these is the carbonyl group which has polymerizing powers of its own (9).

Although it has not been reported that the nitro group influences polymerization, it is quite possible that, like the carbonyl group, it may in some way activate polymerization. It is known that conjugated double bonds along a given carbon chain activate polymerization. The activation of the nitro group may be due to the fact that the nitrogen-oxygen double bond is conjugated with the double bond of the carbon chain.



It is also worthwhile to note that monomers which yield industrially useful polymers have in common with 2-nitrobutene-1 the characteristic $\rangle C=CH_2$ group.

In view of the above facts, it was predicted that 2-nitrobutene-1 would polymerize to form a linear polymer according to the following equation:



$$C_2H_5-\underset{NO_2}{C}=CH_2 \longrightarrow -\overset{C_2H_5}{\underset{NO_2}{C}}-CH_2-\left[\overset{C_2H_5}{\underset{NO_2}{C}}-CH_2\right]_n-\overset{C_2H_5}{\underset{NO_2}{C}}-CH_2-$$

D. Survey of Literature on 1,4-Addition to Nitroölefines

It is known that unsaturated nitro compounds in which the nitro group is conjugated with the ethylenic double bond will undergo 1,4-addition. Several reactions have been carried out to illustrate this additive power of the nitroölefines. Alder (2) has illustrated this by the addition of cyclopentadiene to nitroethylene, 1-nitropropene, 1-nitro-1-pentene, and β-nitrostyrene. All of these added smoothly at 100-110°C. On catalytic hydrogenation the adducts took up one mole of hydrogen with great ease and the resulting compound gave the expected amines with zinc dust and acetic acid. The amine obtained from nitroethylene is endonorbornylamine. This established the adduct as 2-nitro-5-norbornylene and indicated that the reaction was a true diene synthesis. Similarly, the addition of butadiene, methylbutadiene, and 2,3-dimethyl-1,3-butadiene to 1-nitro-1-pentene gave the expected nitro derivatives. Sterically the addition followed the laws which apply generally to the diene synthesis.

Another illustration was given by Worrall (63) in the addition of several aromatic amines to β-nitrostyrene. Several additions were attempted. The aromatic amines which were successfully added to form the β-substituted derivatives of phenylnitroethane were: aniline, p-toluidine, p-aminodiphenylamine, phenylhydrazine, diphenylhydrazine, β-naphthylhydrazine, and tolylhydrazine. Other amines added were: piperidine, semicarbazide, thiosemicarbazide, and ammonia. Phenylenediamine and benzidine reacted with two equivalents of nitrostyrene to form

saturated nitro derivatives. Worrall (63) also found that this type of addition reaction was limited to a comparatively few organic bases because of the tendency of nitrostyrene to form a polymer, and because substituents in the ring of aromatic derivatives have a hindering effect.

Wieland (57) was the first to add aromatic amines to aliphatic unsaturated nitro compounds. By adding aniline to nitroethylene, he was able to isolate N(β-nitroethyl) aniline.

$$CH_2{=}CHNO_2 + C_6H_5NH_2 \longrightarrow C_6H_5NHCH_2CH_2NO_2$$

The addition of several aromatic amines to 2-nitrobutene-1 has been carried out in this laboratory (18). Among the compounds prepared were 2-nitrobutylaniline, N-(2-nitrobutyl)-p-nitroaniline, N-(2-nitrobutyl)-α-naphthylamine, N-(2-nitrobutyl)-p-toluidine and N,N'-Di-(2-nitrobutyl)-o-phenylenediamine.

It has been shown that aromatic amines and hydrazines added readily to α,β-unsaturated nitro compounds containing halogen alpha to the nitro group (62). However, substituted aromatic amines containing negative groups did not react. The addition compound as a rule decomposed as fast as it was formed into halonitromethane and a Schiff base. The latter was decomposed by halonitromethane into benzaldehyde and amine.

The addition compounds of p-toluidine, benzidine, p-phenylenediamine, and phenylhydrazine with bromonitrostyrene have been isolated (62).

Unsaturated nitroölefines such as nitrostyrene and nitrostilbene are capable of 1,4-addition with Grignard reagent (33).

Nitrostilbene reacts with phenylmagnesium bromide as readily as does the corresponding unsaturated ketone - benzaldesoxybenzoin - and like the unsaturated ketone, it forms, apparently exlusively, a 1,4-addition product.

In contrast with the corresponding ketone $(C_6H_5)_2C=C(C_6H_5)COC_6H_5$, the unsaturated nitro compound combined readily with aliphatic magnesium compounds and despite the conjugated system of phenylgroups about the conjugated system, the reaction consisted apparently exclusively of 1,4-addition.

Worrall (65) has carried out several addition reactions with dinitrovinylbenzene. The bromination of this compound gave 1,4-bis(β-bromo-β-nitrovinyl)benzene. When heated, the dinitrovinylbenzene added aniline to give 1,4-bis(α-anilino-β-nitroethyl)benzene. Although dinitrovinylbenzene may form an addition compound with ammonia, the principal product was an amorphous polymer of the former which decomposed slowly above 300°C.

Flürscheim (15) found that 2-bromo-2-nitro-1-p-nitrophenylethylene underwent partial addition at its double bond of a molecule of alcohol on mere recrystallization from this solvent. The corresponding o-nitro compound reacted similarly, though less readily. Several nitroölefines were tested with varying degrees of success.

Flürscheim (15) suggested, and cited proof, that the above reaction took place through a slow initial 1,4-addition of alcohol to yield an isonitro-compound, followed by two competing rapid reactions, viz., reversal of the addition, whereby the

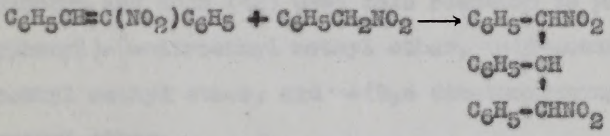
nitroölefine was regenerated, and stabilization of the addition product by rearrangement of its isonitro form to the "true" nitroethoxyethane derivative.

When bromine was added to 1-bromo-1-nitrobutene-1 or 1-bromo-1-nitropentene-1, the resulting saturated tribromonitrohydrocarbon was not stable and split off hydrogen bromide (35). When potassium hydroxide in cold methyl alcohol reacted with 1-bromo-1-nitrobutene-1 and 1-bromo-1-nitropentene-1, the methyl alcohol addition product with the methoxyl group on the 2-carbon atom was obtained. However, potassium hydroxide in hot methyl alcohol gave the salts of 1,1-dinitro-2-methoxybutane and 1,1-dinitro-2-methoxypentane. The free compounds could not be isolated in the pure form because they deflagrated on distilling in vacuo. Since both potassium bromide and potassium nitrite were identified in the reaction mixture, it is probable that some of the nitrobromoölefines decomposed, liberating potassium nitrite which then reacted with some unchanged nitrobromoölefine to form the dinitro compound. Addition of ammonia to the above unsaturated compounds gave 1-bromo-1-nitro-2-aminobutane and pentane which were very unstable. The aniline and piperidine derivatives could not be obtained pure because of their decomposition on distillation in vacuo, and the methyl and ethyl amines could not be isolated, although the disappearance of the penetrating odor indicated that the addition had taken place.

Lovenich (34) found that the introduction of a phenyl group on the 2-carbon atom of the nitrohaloölefines showed an even less

tendency to add negative atoms or groups, and on the other hand, a greater tendency to add positive groups. On addition of ammonia and piperidine to 1-bromo-1-nitro phenylethylene, it was possible to isolate the corresponding free amines. With aniline in ether, there was a color change, pointing to addition, but in a very short time, even in the cold, aniline hydrobromide and 1-nitro-2-phenylacetylene were split off. 1-Bromo-1-nitro-2-amino-2-phenylethylene which was formed by the addition of ammonia to 1-bromo-1-nitro phenylethylene underwent an intramolecular cleavage into ammoniumbromide and 1-nitro-2-phenylacetylene, on long standing. On the other hand, 1-bromo-1-nitro-2-piperidino-2-phenylethane was entirely stable, although its hydrochloride decomposed in water to form 1-nitro-1-bromo phenylethane and piperidine hydrochloride. The diethylamine addition product could not be obtained.

The addition of substituted nitroparaffins to a substituted nitroölefine has been reported by Heim (28).



$$C_6H_5CH{=}C(NO_2)C_6H_5 + C_6H_5CH_2NO_2 \longrightarrow \begin{array}{l} C_6H_5\text{-}CHNO_2 \\ \qquad | \\ C_6H_5\text{-}CH \\ \qquad | \\ C_6H_5\text{-}CHNO_2 \end{array}$$

The unsubstituted nitroparaffins also reacted as shown by the production of dinitroneopentane from 1-nitro-2-methylpropene and nitromethane (23).

Nitroölefines are readily hydrolyzed by the action of dilute sulfuric acid as follows (51):

$$RCH=C(NO_2)R' + H_2O \xrightarrow{H_2SO_4} RCHOHCHNO_2\ R'$$

$$RCHOHCHNO_2R' \longrightarrow RCHO + RCH_2NO_2$$

$$2R'CH_2NO_2 + 2H_2O + H_2SO_4 \longrightarrow 2R'COOH + (NH_3OH)_2SO_4$$

Askenasy and Meyer (3) had previously reported small amounts of acrylic acid from the hydrolysis of 1-nitropropene. In the first step of this reaction water functions as the compound containing active hydrogen.

Friedländer and Mähly (16) found that potassium ethoxide added to p-nitro-ω-nitrostyrene, when dissolved in an alcoholic solution of potassium hydroxide, formed $O_2NC_6H_4CH(OC_2H_5)CHNO_2K$.

Meisenheimer and Heim (36, 37) and Rosenmund (43) reported that ω-nitrostyrene added sodium methoxide or ethoxide instantaneously as follows:

$$C_6H_5CH=CHNO_2 + NaOCH_3 \rightarrow C_6H_5CH(OCH_3)CH=NO_2Na$$

The resulting solution was unstable and yielded $C_6H_5CH(OCH_3)CHNO_2-CH(C_6H_5)-CH_2NO_2$.

Reichert and Koch (42) used this reaction to prepare α-(2-methoxyphenyl)-β-nitroethyl methyl ether, α-(4-methoxyphenyl)-β-nitroethyl methyl ether, and α-(3,4 dimethoxyphenyl)-β-nitroethyl methyl ether.

The addition of acetone to 1-nitro-2-methylpropene yielded 5-nitro-4,4-dimethyl-2-pentanone (4).

$$CH_3COCH_3 + (CH_3)_2C=CHNO_2 \longrightarrow O_2NCH_2-C(CH_3)_2CH_2COCH_3$$

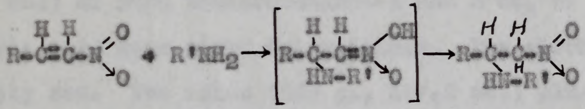
An interesting addition reaction which might be mentioned in this connection is that postulated by Holleman (30) to explain the changes observed when ω-nitrostyrene was treated with

potassium cyanide and then acidified. Before the formation of bimolecular condensation products, he postulated the reaction:

$$C_6H_5CH{=}CHNO_2 + KCN \longrightarrow C_6H_5CH(CN)CH{=}NOOK$$

Upon acification, hydrocyanic acid split out between two molecules and a bimolecular product resulted.

2-Nitrobutene-1 is an unsaturated nitro compound containing a conjugated unsaturated system and accordingly is capable of 1,4-addition. There seems to be no reason to doubt that amines react with 2-nitrobutene-1 in this manner. The reaction is postulated as taking place by an initial 1,4-addition and subsequent rearrangement of the aci-nitroparaffin.



where R is either an aryl or an alkyl group and R' is either an aromatic or an aliphatic group. The reaction starts through the mobile hydrogen of the amino group which, because of its chemical affinity for oxygen, becomes linked to that element. The rest of the molecule attaches itself to the carbon, more remote from the nitro group. The resulting unsaturated pseudo acid is of an unstable type; hence, it spontaneously rearranges into a saturated nitro derivative, the substance actually isolated.

The above search of literature indicates that no attempts have been made to add aliphatic amines to aliphatic unsaturated nitro compounds. Therefore, in this paper a study of the synthesis of nitroalkyl amines by the addition of aliphatic amines to nitroölefines will be reported.

II. EXPERIMENTAL

A. Preparation of 2-Nitrobutene-1

The procedure patented by Schwarz and Nelles (46) and modified by Mason and Gitchel (18) was believed to be the best method for the preparation of 2-nitrobutene-1.

The crude 2-nitrobutyl alcohol was distilled, and the fraction boiling at 120-122°C. at 20-23 mm. was collected.[1] A three-necked flask was equipped with thermometer, mechanical stirrer, dropping funnel and reflux condenser. Two moles (238 g., 211.2 cc.) of pure 2-nitrobutanol-1 and 3 cc. of concentrated sulfuric acid were mixed in the flask. The alcohol turned slightly red. Two moles (204 g., 187.2 cc.) plus 5 cc. excess of technical acetic anhydride were added at such a rate as to maintain a temperature of 60-62°C. This reaction was very exothermic and required about one and a half to two hours. The reaction mixture was then heated on the steam-bath for about a half hour. An attempt was made to wash the compound with water, but it proved to be quite miscible. The addition of a 20% salt solution did not cause a complete separation. An amount of sodium bicarbonate equivalent to the sulfuric acid present was

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[1] The Commercial Solvents 2-nitrobutyl alcohol, Lot D-2037, gave about 68-70% of the pure nitroalcohol, but another sample, Lot D-5867-3, gave yields around 30-40%. Considerable low boiling material and much residue were found in the latter crude product.

dissolved in a 20% salt solution and added slowly. The two layers separated readily when the acid had been neutralized. Washing was continued with a 20% salt solution. The ester was dried over anhydrous calcium chloride. The dried product was distilled under reduced pressure. Most of the ester distilled at 110°C. at 15 mm. pressure and the yield was 250 g. or 78.5% 71%. The low yield was due to considerable loss in washing. Later preparations by this method gave yields as high as 80%.

In a 500 cc. flask was placed 1.05 mole (169.1 g.) of the pure 2-nitrobutylacetate and 0.6 g. of solid sodium hydroxide was added. The flask was equipped with a thermometer at the side arm and one in the reaction mixture. The apparatus was arranged for distillation under reduced pressure and the mixture was heated in an oil-bath. The oil-bath was kept at 105-115°C. When the reaction mixture reached 95°C., a slight exothermic reaction took place and the pressure was lowered to 109 mm. The temperature rose to 103°C. and then slowly dropped to 95°C. During this time the liquid distilled at 72-76°C., bath temperature 113-117°C. At the end of one and a half hours the reaction temperature had dropped and the distillation was very slow, so the reaction was stopped. The pale green distillate was washed repeatedly with a saturated solution of salt containing about 5% sodium carbonate until all the acetic acid was removed. The 2-nitrobutene-1 was dried over anhydrous calcium chloride and distilled at 60°C. at 42 mm. The yield from the 2-nitrobutyl acetate was 60.4 g. or 57%. Later preparations from the 2-nitro-

butyl acetate gave yields as high as 70-75%.

The above process for preparing the nitroölefine proved to be quite long. The washing of the acetate and the removing of the acetic acid from the final product were time-consuming and the extreme lacrimatory effect of the 2-nitrobutene-1 made this a very disagreeable task. In an attempt to shorten some of these steps, the following method for the preparation of 2-nitrobutene-1 was found to be much simpler and gave considerably higher yields.

One part of the crude 2-nitrobutyl alcohol and 0.1 part of powdered anhydrous magnesium sulfate were placed in a flask. After standing overnight, the mixture was placed in a Claisen flask and distilled at 50 mm., bath 150-160°C. The 2-nitrobutene-1 and water distilled over between 50 and 70°C. The two layers were separated by adding a small amount of sodium chloride. When dried over anhydrous calcium chloride, the 2-nitrobutene-1 distilled at 59-61°C. at 42 mm. The yield was 75%.

B. Effect of Various Catalysts on the Polymerization of 2-Nitrobutene-1

Although nitroethylene polymerizes readily at room temperature, without the addition of any catalyst, it was found that 2-nitrobutene-1 could be kept at room temperature for three or four days before any noticeable polymerization occurred. Consequently, an attempt was made to find suitable catalysts for the polymerization.

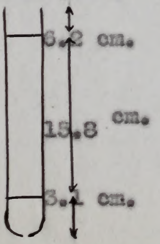
Several prospective catalysts were chosen on the basis of their effective action on the polymerization of unsaturated and conjugated systems.

It is known that the more desirable long-chain polymers are formed at low temperatures. These catalysts were therefore tested at room temperature according to the following procedure.

1. Miscellaneous Catalysts

Ten cubic centimeters of the freshly prepared nitroölefine were placed in a test tube and 0.1 g. of the catalyst was added. The tubes were stoppered tightly and shaken vigorously to insure complete dispersion of the catalyst.

In order to check on the effectiveness of the various catalysts, a simple viscosity tube similar to the one in the figure below was used.



Volume - 6.9 cc.
Diameter - 10.0 mm.
Water at 27°C. - 14.1 sec.

The polymerizing substance was placed in the viscometer and the time of flow was recorded in seconds by a stop watch. The following results indicate the effectiveness of the catalysts. Since 2-nitrobutene-1 polymerizes slowly on standing, the control was tested each time. In the several columns of Table I, the figures represent the number of seconds required for 6.9 cc. of the sample to flow through the viscometer. The letters represent the solubilities and color changes noted. The data in column A represent the observations made immediately after adding the catalyst; in column B, the observations after standing 2.5 hours; column C, after standing two days; column D, after standing four days; column E, after standing several days.

TABLE I

Catalyst	Grade	A	B	C	D	E
Ammonium Persulfate	C.P.	13.6 i.	14.1 lb	13.6 lb	14.0 lb	14.0 gb
Benzoyl Peroxide	Kodak Tech.	13.5 s.	13.6 nc	14.1 nc	14.0 lg	14.0 lb
Sulfuric Acid	C.P. Conc.	13.6 s. br	14.0 b	14.0 lr	13.4 lr	14.0[4] ly
Aluminum Chloride	C.P.	13.6 ss. lb	13.8 lb	∞[1] lb	14.0[2] lb	14.0 b
Pyridine	Tech.	13.6 s.	16.8 db	85.0[3] db	84.0 db	85.0 db
Control	Freshly prep.	13.6	13.6 lg	13.6 lb	13.6 lb	13.6 lb
		Temp.- 26°C.	Temp.- 24°C.	Temp.- 19°C.	Temp.- 24°C.	Temp.- 28°C.

i. - insoluble
s. - soluble
ss. - slightly soluble
l. - light
d - dark
b - brown
g - green
r - red
y - yellow
nc - no change

1. After two days the nitrobutene and aluminum chloride formed a very hard translucent compound which would not flow from the test tube. On examining with a stirring rod, it was found that the hard material was a thick shell enclosing unpolymerized nitrobutene. The product was too gelatinous to flow through the viscometer. The lacrimatory power had decreased considerably.

2. On standing, the solid particles dissolved. More aluminum chloride was added without causing any further change.

3. After two days at room temperature the 2-nitrobutene-1 catalyzed with pyridine had formed a cherry brown viscous polymer. The sharp odor had disappeared and a faint odor of burnt sugar or molasses was very evident. On standing, further polymerization could not be detected by the viscometer.

4. After seven days the 2-nitrobutene-1 catalyzed with sulfuric acid had a small amount of red viscous non-miscible material on the bottom of the test tube. The solution had turned slightly yellow. It is possible that the small amount of sulfuric acid had reacted with an equivalent amount of the 2-nitrobutene-1 and had settled to the bottom, leaving the 2-nitrobutene-1 uncatalyzed.

Aside from the peculiar reaction of aluminum chloride, the only active catalyst at room temperature in this experiment was pyridine.

2. Heat as a Catalyst

Heat frequently catalyzes polymerization, but a desirable product is seldom obtained at high temperatures. To determine the effect of heat on 2-nitrobutene-1, about 10 cc. were placed in a test tube and left in a steam-bath. At this temperature polymerization proceeded rapidly and within three days a very viscous liquid was observed. After seven days the polymer was a very black thermoplastic material. When molded on a stirring rod, it tended to remain thermoplastic after cooling. After several days it could be broken loose from the glass rod but was still thermoplastic. A rod dipped into the hot polymer and pulled out slowly formed very long, thin, black threads which did not tend to stick together when wound on a glass rod. On long cooling, they tended to become somewhat brittle. (Possibly a plasticizer would make them sufficiently flexible and lend strength.) In ten days the polymer was quite brittle and could be ground to a powder in a mortar. The powdered polymer was also thermoplastic.

3. Other Miscellaneous Catalysts

In the previous experiment it has been shown that 2-nitrobutene-1 will polymerize to a solid when subjected to heat for some time. The purpose of this experiment was to test several more catalysts in an attempt to prepare a more suitable solid polymer at room temperature. The following table indicates the catalysts chosen and their effectiveness. These catalysts were tested according to the procedure given above.

TABLE II

Catalyst	Grade	A	B	C	D	E
Trichloracetic acid	Kodak tech.	lb	nc	b	rb	rb[1]
Benzal acetone	Student prep.	nc	nc	lb	lb	lb[2]
Sodium	Freshly cut	c	nc	lb	b mv	b[3]
Aluminum chloride	C.P. dry	db-heat	nc	lb	lg	b[4]
Sodium hydroxide	C.P. pellets	nc-i.	nc	lb[5]	lb mv	b v
Titanium hydride		lg		lb	lb	b

l - light
d - dark
b - brown
r - red
c - cloudy
nc - no change
g - green
v - viscous
mv - more viscous
i. - insoluble

A - observations on adding catalyst
B - observations after standing 2 days
C - observations after standing 5 days
D - observations after standing 10 days
E - observations after standing 17 days

The viscosity was not tested since observation showed very little change. A comparison of colors seemed to be satisfactory to distinguish between the effectiveness of these catalysts and thus eliminated the unpleasant task of viscosity measurements on a lacrimator.

1. The trichloracetic acid has some effect, as indicated by the change of color. The viscosity increased somewhat, but not as much as in the case of pyridine.

2. The benzalacetone had little or no effect at room temperature.

3. The sodium was freshly cut and placed in the test tube in one piece. The solution was noticeably more viscous. Sodium would probably be much more effective in smaller particle size suspended in the solution in order to increase surface area and cause more intimate contact.

4. The experiment with aluminum chloride was rechecked. This time heat was liberated on adding and a slightly viscous compound formed very soon. After standing, the light green color returned to the liquid.

5. After five days, very little change was noticed with solid sodium hydroxide. The sodium hydroxide would not stay in suspension. Some stearic acid was added to cause an emulsion, which helped somewhat, but the tube had to be shaken frequently to maintain the emulsion. The viscosity increased noticeably in the next five days.

Of the above catalysts, sodium and sodium hydroxide appeared to be the only active catalysts.

4. Amines as Catalysts

Pyridine was found to be a satisfactory catalyst for the formation of a liquid polymer. Since pyridine is an amine, it was believed that other amines might be active in the formation of a more suitable polymer.

The following amines were tested, using 5 cc. of 2-nitrobutene-1 and 0.05 g. of catalyst.

TABLE III

Amines	A	B	C
Urea	no change	no change	small amount of yellow, sticky substance
Acetamide	no change	slightly darker	light brown
2,4-Dinitrophenylhydrazine	no change	light orange	light brown
Diphenylamine	no change	brown	brown
Ammonium acetate	no change	red	dark red, slightly viscous
Diethylamine	violent exothermic reaction. Red.	red, viscous solution	red, viscous solution
Dicyclohexylamine	very violent exothermic reaction leaving viscous liquid	black semi-solid polymer	black solid polymer similar to one formed by heat
Dimethylaniline	no change	dark brown	dark brown, slightly viscous

A - observations on adding amine
B - observations after standing 2 days
C - observations after standing 9 days

Of the above compounds tested, diethylamine and dicyclohexylamine formed viscous polymers. The reactions were extremely exothermic and with dicyclohexylamine a solid polymer was formed. 2-Nitrobutene-1 catalyzed with urea formed a very small amount of yellow, sticky polymer after standing for nine days.

This experiment verified the fact that amines tend to catalyze this polymerization. However, polymers more suitable than those catalyzed by heat and pyridine were not formed.

5. Aluminum Chloride as a Catalyst

Since different observations were made in the two experiments in which aluminum chloride was used (see Tables I and II), another test was made with this catalyst. All reagents were dry and the reaction mixture was placed in a desiccator. The reaction mixture turned brown on adding aluminum chloride and heat was liberated. After two days a solid brown polymer was formed. The reaction mixture was then exposed to air and the compound became liquid after seven days.

6. Sodium Hydroxide as a Catalyst

A preliminary test showed that 2-nitrobutene-1 polymerized into a yellow, sticky mass when heated with sodium hydroxide. An experiment was devised to test the polymers formed under varying concentrations of sodium hydroxide at 35°C. and room temperature.

Three cubic centimeters were placed in a six-inch test tube and one cubic centimeter of sodium hydroxide solution was added. The mixture was stoppered, shaken and placed in a 35° constant temperature bath or at room temperature. The sodium hydroxide and 2-nitrobutene-1 were not miscible. The following tables show the effect of temperature and concentration of catalyst on the reaction and the final product.

TABLE IV

Polymerization of 2-Nitrobutene-1
by Sodium Hydroxide at Room Temperature

Concentration of Sodium Hydroxide (%)	Two Days	Five Days	Eight Days
0.1	very little change	no change	light yellow solution
0.5	very little change	no change	light yellow solution
1.0	very small amt. of solid yellow, sticky pol.	no change	small amt. of brown pol.
3.0	very small amt. of solid yellow, sticky pol.	small amt. of polymer	small amt.of brown pol.
5.0	1/8 polymerized	small amt. of polymer	viscous pol.
7.0	1/5 polymerized	slight increase in amt. of polymer	slightly less polymer
10.0	red, viscous layer on bottom	2/3 solid pol.	slightly less polymer
15.0	red, viscous layer on bottom	completely polymerized, solid yellow polymer	slightly less polymer

After two days it was noticed that the greatest amount of polymerization had taken place in the tubes containing 5, 7, and 10% sodium hydroxide. The polymer was yellow and sticky, and seemed to be formed from a liquid polymer which was surrounding it.

On the fifth day it was noted that an increasing amount of polymer was forming with an increase in the concentration of sodium hydroxide from 3% to 15%.

With concentrations of sodium hydroxide greater than 7%, a decrease in the amount of polymer on long standing was noted.

TABLE V

Polymerization of 2-Nitrobutene-1
With Sodium Hydroxide Catalyst at 35° C.

Conc. Sodium Hydroxide (%)			
0.1	no change	no change	light brown
0.5	no change	very light brown	light brown
1.0	yellow	light brown	brown, slightly viscous
3.0	yellow	brown, viscous	brown, viscous
5.0	small amt. of polymer	brown, very viscous	brown, very viscous
7.0	1/2 polymerized solid	complete polymerization	complete polymerization
10.0	1/2 polymerized solid	complete polymerization	complete polymerization
15.0	red, viscous liquid	complete polymerization	complete polymerization

From these experiments it was evident that the rate and degree of polymerization were directly effected by the tempera-

ture and the concentration of the sodium hydroxide solution. The solid polymers formed more slowly at room temperature than at 35°C. The hardness of the product obtained also varied directly with the concentration of sodium hydroxide used and the temperature at which the reaction was carried out.

At 35°C., the polymer formed after two or three days with 7% sodium hydroxide was quite soft. With 10% sodium hydroxide solution, the polymer was a light yellow, taffy-like substance. The latter could be stretched considerably but had no elasticity. The polymer formed in 15% sodium hydroxide solution was yellow and more firm than the previous ones. It still had the taffy-like appearance and characteristics. Upon cooling, this polymer became slightly brittle.

From the previous experiments it was found that the most suitable liquid polymer was formed by pyridine and the best solid polymer was formed by 10 to 15% sodium hydroxide solution at 35°C.

An attempt was then made to study these two polymers.

7. Pyridine as a Catalyst (First Test)

The liquid polymer has been previously prepared from 2-nitrobutene-1 with 0.1% of pyridine by allowing the mixture to stand at room temperature for two or three days. This procedure was repeated, using 45 cc. of 2-nitrobutene-1 and 4.5 cc. of pyridine. After thoroughly mixing, the container was allowed to stand. In about ten minutes an exothermic polymerization started.

The reaction became so violent that the main portion of the contents of the flask was blown out and fire followed. A charred residue was left.

8. Pyridine as a Catalyst (Second Test)

Another attempt was made to prepare the liquid polymer by using pyridine as a catalyst. This time .25 g. of pyridine and 25 g. of 2-nitrobutene-1 were used. The mixture darkened slightly after adding the pyridine, but no heat was evolved. After three days the polymer had reached its maximum viscosity.

9. Pyridine as a Reactant

It was believed that the pyridine might react with the 2-nitrobutene-1. On this basis .1 mole (7.91 g.) of pyridine and .1 mole (10.1 g.) of 2-nitrobutene-1 were allowed to react. The pyridine was added dropwise to the 2-nitrobutene-1. After 3 g. had been added, an exothermic reaction started. The temperature was allowed to reach 50°C., and was then cooled in an ice-bath. Further addition did not cause much rise in temperature.

The product was placed in a 125 cc. Claisen flask and distillation was attempted. About 6.5 g. of a clear liquid, which proved to be pyridine, distilled below 50°C. at a 10 mm. pressure.

When the bath reached 125°C., an apparent exothermic reaction started. The oil-bath was removed, and the reaction continued

for some time. Upon cooling, the residue was found to be a very dark brown, viscous material.

The oil bath was replaced and distillation continued. About 5 g. distilled over at 79-80°C., 5 mm., bath 155°C. This wasan oily red liquid, much less viscous than the non-volatile material. On heating the bath to 165°C., the residue completely decomposed, leaving a charred mass. It was concluded that pyridine acted as a catalyst for the polymerization, and did not react with the 2-nitrobutene-1.

10. Reduction of Liquid Polymer

The pyridine and unpolymerized nitrobutene were removed by distillation at 5 mm. pressure from the polymer prepared in the first test of using pyridine as a catalyst (0.25 g. pyridine and 25 g. 2-nitrobutene-1). The residue was a viscous, brown material.

If the nitrobutene polymerizes as predicted, hydrogenation should produce a polyamine which might have a lower boiling point and could be distilled.

Twelve grams of the material were dissolved in 150 cc. of 95% alcohol and 10 g. of Raney nickel were added. The hydrogenation was started at 20-pounds pressure and later increased to 40-pounds pressure. The hydrogenation was quite exothermic and a fair amount of hydrogen was consumed. The alcohol was removed through an 18-inch fractionating column by a steam-bath. The alcohol distilled at about 70°C. It is quite possible that confor some time. Upon cooling, the residue was found to be a very dark brown viscous product.

The oil bath was replaced and distillation continued. About 5 g. distilled over at [illegible], 4 mm., bath 160°C. This fraction was liquid, much less viscous than the non-volatile residue. [illegible] the residue completely [illegible], leaving a charred mass. It was concluded that [illegible] acted as a catalyst for the polymerization, [illegible]

10. The Action of [illegible]

The [illegible] were [illegible] by distillation of [illegible] from the polymer prepared in the [illegible] as a catalyst [illegible]. The residue was a viscous, brown material.

If the [illegible] polymerization is prohibited, hydrogenation should produce a polymer which might have a lower melting point and could be distilled.

Thirty grams of the material were dissolved in 120 cc. of [illegible] and 10 g. of Raney nickel were added. The hydrogenation was started at [illegible] pressure and later increased to [illegible] pressure. [illegible] hydrogen was absorbed. The alcohol was removed through [illegible] column by [illegible]. The residue distilled at above [illegible]. It is quite certain that some siderable secondary butylamine was formed which has a very low boiling point and would pass over with the alcohol.

The residue was more viscous than the original material, and no attempt was made to distill it.

The original liquid polymer gave the Baeyer test for unsaturation in benzene solution after standing three months. Since the product was reduced over Raney nickel, the unsaturation should remain in the reduced compound. The Baeyer test proved this to be true.

When warmed with 15% sodium hydroxide solution, the original liquid polymer dissolved. The alkaline solution was neutralized with hydrochloric acid and the polymer reappeared. This behavior could easily be explained if the polymerizing compound had been nitroethylene on the basis of the activated hydrogen. The predicted structure of this polymer did not indicate solubility in sodium hydroxide nor predict a positive Baeyer test. However, it is possible that the chain of the polymer may end with a nitro group on a secondary carbon atom. If this is true, the one salt-forming nitro group may be sufficient to cause solubility of the whole chain.

A small portion of the reduced polymer proved to be only slightly soluble in sodium hydroxide. The reduced polymer, when warmed with hydrochloric acid, was quite soluble but was not precipitated by sodium hydroxide.

11. Solubility of Solid Polymer

The polymer formed at 35°C. with 10% sodium hydroxide was washed free of sodium hydroxide with dilute acetic acid and then washed with water. The resulting polymer was light yellow with taffy consistency.

When pressed in a thin sheet, small hard lumps were noticeable. Perhaps these are polymers of nitropropylene, nitropentene, or higher molecular weight polymers formed because of closer contact with the catalyst.

The solubility of the polymer was tested with the following results:

1. Acetone - very soluble - yellow solution
2. 15% Sodium Hydroxide - insoluble - soluble on heating
3. 95% Ethyl Alcohol - insoluble
4. Carbon Tetrachloride - insoluble
5. Dioxane - soluble - yellow solution
6. Toluene - soluble - yellow solution
7. Ethyl Acetate - soluble - yellow solution
8. Benzene - soluble
9. Ether - slightly soluble

Several catalysts, such as benzoyl peroxide and ammonium persulfate, which are known to be very effective in the polymerization of conjugated systems, have been shown to have little or no effect on 2-nitrobutene-1. However, several organic and inorganic bases have proved to be successful catalysts.

From the above experiments it can be seen that 2-nitro-

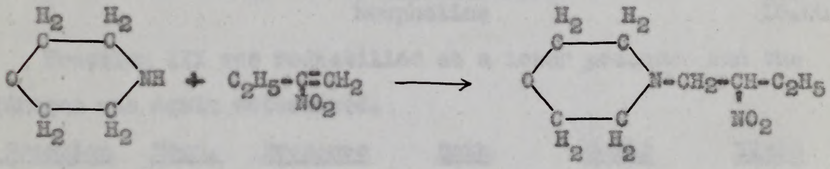
butene-1 polymerizes to form polymers varying in composition from light oils to solids. The type of polymer depends very largely on the catalyst chosen. However, temperature has been shown to affect the product.

Although pyridine reacts as a catalyst, it is possible that other amines might form an addition product.

C. Addition of Amines to 2-Nitrobutene-1

Although other workers have found that certain aromatic amines will add to nitroölefines such as nitrostyrene, and also to aliphatic nitroölefines such as 2-nitrobutene-1, no reference has been found to the addition of either a heterocyclic amine or an aliphatic amine to a nitroölefine. In view of this fact, an attempt was made to isolate the addition products from the reactions of 2-nitrobutene-1 with morpholine, piperidine, diethylamine, and n-dibutylamine.

1. Morpholine (First Preparation)



To 0.178 mole (18 g.) of freshly prepared 2-nitrobutene-1 was added the theoretical amount (15.51 g.) of recently distilled morpholine at such a rate that the temperature was maintained between 50 and 60°C. The very exothermic reaction resulted in an orange-yellow oil. No odor of the severely lacrimatory nitroölefine could be noted.

The reaction mixture was distilled in a 125 cc. asbestos-insulated Claisen flask with the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I*	75°C.	14.5 mm.	145°	Clear	1.5 g.
II	75-125°C.	14.5 mm.	145-150°	Light yellow	0.5 g.
III	125-135°C.	14.5 mm.	150-155°	Light yellow	25.5 g.

Yield - 25.5 g. or 76.1%

*A reddish crystalline solid formed in condenser and was removed by applying steam in condenser jacket.

A nitrogen determination on Fraction III indicated that the compound was not pure.

% N Found		% N Calculated	
14.01	13.89	1-Morpholino-2-nitrobutane	14.89
		2-Nitrobutene-1	13.84
		Morpholine	16.08

Fraction III was redistilled at a lower pressure and the nitrogen was again determined.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	115-119°C.	.6 mm.	150°	Light yellow	1.5 g.
II	119-122°C.	.6 mm.	150-165°	Light yellow	22.0 g.

A more accurate boiling point determination showed that the pure compound was a light yellow oil boiling at 120-121°C., at 0.6 mm., bath 150-155°C. Nitrogen determinations on Fraction II showed that this is the desired product.

% N Found		% N Calculated	
14.78	14.71	1-morpholino-2-nitrobutane	14.89
		2-nitrobutene-1	13.84
		morpholine	16.08

Since 1-morpholino-2-nitrobutane has a tertiary amine group, the picrate should form. It was found that the picrate formed readily and could be recrystallized from 95% alcohol. The puri-

fied product, after recrystallizing twice from alcohol, was a bright yellow needle-like crystalline product melting at 125-126°C.

The picrate was analyzed for nitrogen with the following results:

% N Found		% N Calculated	
16.69	16.40	1-morpholino-2-nitrobutane picrate	16.79

Zief and Mason (67) first prepared the compound by condensing morpholinemethanol with 1-nitropropane. The boiling point was recorded as 134-136°C., at 15 mm. pressure. The picrate of this compound was made and its melting point recorded at 120-121°C. It was found in this work that the picrate melted at 125-126°C., after recrystallizing twice from alcohol.

2. Morpholine (Second Preparation)

To 0.2 mole (20.42 g.) of 2-nitrobutene-1 in a 125 cc. Erlenmeyer flask was added an equal molecular quantity (17.42 g.) of morpholine at such a rate that the temperature was maintained at 60-65°C. The reaction proved to be very exothermic as before and the reaction mixture was a reddish yellow. (Note - If carried out at 40 or 50°C., the amount of polymerization might be decreased and the yield of the desired product increased.) The reaction mixture was distilled with the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I	106°C.	12 mm.	165°	Reddish yellow	1.2 g.
II	106-125°C.	12 mm.	185°	Light yellow	1.3 g.
III	125-132°C.	12 mm.	185-193°	Light yellow	32.1 g.

The 32.1 g. obtained from 37.84 g. of reaction mixture represents an 84.8% yield.

Fraction III was analyzed for nitrogen.

% N Found	% N Calculated	
14.40 14.32	1-morpholino-2-nitrobutane	14.89

Fractions II and III of the previous distillation were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	102°C.	16 mm.	165°	Light yellow	0.2 g.
II	102-134°C.	15 mm.	165-180°	Light yellow	1.0 g.
III	134-138°C.	15 mm.	185-190°	Light yellow	29.8 g.

After the second fractionation, the yield was reduced from 84.8% to 78.8%. A nitrogen determination was made on Fraction III and found correct for 1-morpholino-2-nitrobutane.

% N Found	% N Calculated	
14.78 14.69	1-morpholino-2-nitrobutane	14.89

An accurate boiling point determination in a 125 cc. Claisen flask proved that the compound boiled at 135-138°C., (137-139°C. corrected), 15 mm., bath temperature 185-190°.

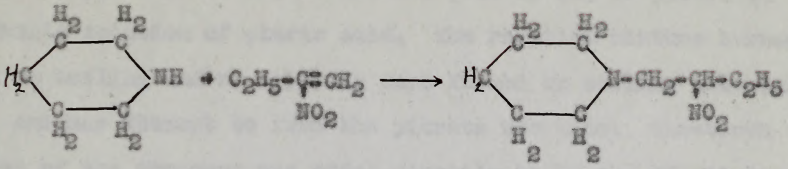
The picrate was easily prepared and recrystallized from 95% ethyl alcohol. After the first recrystallization the melting point was found to be 125-126°C. A mixed melting point was made using a fifty-fifty mixture of picric acid and the prepared picrate. An irregular melting point having a range of 100-115° indicates that this compound is not picric acid.

The picrate was recrystallized a second time and the melting point remained constant.

A nitrogen determination was correct for 1-morpholino-2-nitrobutane picrate.

% N Found		% N Calculated	
16.50	16.42	1-morpholino-2-nitrobutane picrate	16.79

3. Piperidine (First Preparation)



To 0.215 mole (22 g.) of freshly prepared 2-nitrobutene-1 were added 0.215 mole (18.31 g.) of recently distilled piperidine. The reaction was very exothermic and the rate of addition had to be very slow in order to keep the reaction below 70°C. The product is a light red oil.

The reaction mixture was placed in a 125 cc. Claisen flask and distilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I*	100-110°C.	13.1 mm.	150-160°	Yellow	2.0 g.
II	110-120°C.	13.1 mm.	150-170°	Yellow	33.2 g.

Yield - 33.2 g. or 82.5%

*Fraction I contained a very small amount of yellow solid.

Fraction II was redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	110°C.	11.0 mm.	157°	Yellow	2.0 g.
II	110-115°C.	10.3 mm.	155-160°	Yellow	29.2 g.

Yield - 29.2 g. or 72.5%

A nitrogen determination was correct for 1-piperidino-2-nitrobutane.

% N Found		% N Calculated	
14.81	14.50	1-piperidino-2-nitrobutane	15.04
		2-nitrobutene-1	13.84
		piperidine	16.85

An attempt was made to prepare the picrate (47) using 0.1 g. of the compound in 20 cc. of alcohol plus 20 cc. of saturated alcoholic solution of picric acid. The reaction mixture turned dark on boiling and no crystals were formed on cooling overnight.

Another attempt to form the picrate was made. One-tenth of a gram of the compound was added directly to 20 cc. of saturated picric acid solution (in 95% alcohol). The mixture was boiled gently for a very short time. Crystals formed after cooling. The picrate was slowly soluble in hot alcohol. Recrystallization yielded bright yellow crystals melting at 137-138°C. A nitrogen determination was correct for 1-piperidino-2-nitrobutane picrate.

% N Found				
16.48	16.29	16.52	1-piperidino-2-nitrobutane picrate	16.54
			1-piperidino-2-nitrobutane	15.04
			picric acid	18.34

4. Piperidine (Second Preparation)

The second preparation was carried out using 0.2 mole (17.03 g.) of piperidine and 0.2 mole of 2-nitrobutene-1 (20.42 g.). The temperature was kept at 60-62°C. by controlling the rate of addition.

The resulting orange-red oil was distilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	105°	15 mm.	140°	Reddish	0.5 g.
II	105-112°C.	14 mm.	150°	Light brownish yellow	31.5 g.
III	112-117°C.	14 mm.	154°		

Yield - 31.5 g. or 84.1%

Fractions II and III were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	110°C.	15 mm.	155°	Light yellow	0.7 g.
II	110-117°C.	14 mm.	160°	Light yellow	1.2 g.
III	117-121°C.	14 mm.	154-161°	Light yellow	30.0 g.

Yield - 30.0 g. or 80.1%

The compound was light-colored, but changed to a light red after standing. A boiling point determination showed that the pure compound boiled at 117-120°C. (118-121°C. corrected), 14 mm., bath 155-160°C.

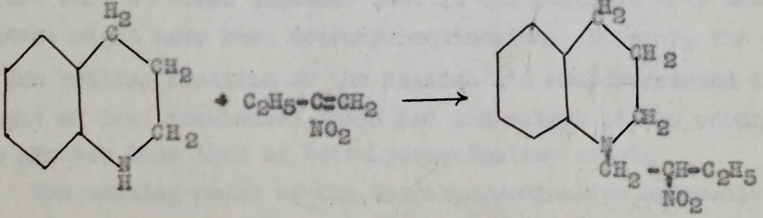
A nitrogen determination was correct for 1-piperidino-2-nitrobutane.

% N Found	% N Calculated	
16.42 16.15	1-piperidino-2-nitrobutane	16.54

The picrate was prepared as in the previous preparation and recrystallized twice from alcohol. The bright yellow needle-like crystals melted at 137-138°C.

Cerf de Mauny (11) has prepared this compound by the condensation of piperidine, formaldehyde, and 1-nitropropane. The recorded boiling point is 128-133°C., at 18 mm. pressure.

5. Tetrahydroquinoline (First Preparation)



To 0.178 mole of 2-nitrobutene-1 (18.2 g.) was added an equal molecular quantity (23.7 g.) of 1,2,3,4-tetrahydroquinoline. The reaction was exothermic but much less heat was evolved than in the case of piperidine and morpholine. Very little rise in the temperature was noted until about 5 g. of the tetrahydroquinoline had been added. The temperature then rose rapidly to 60°C. This temperature was maintained by controlling the rate of addition. The crude product was a very viscous, orange-red oil.

About half of the material (21 g.) was placed in a Claisen flask, well insulated with asbestos and fractionated.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	96°C.	2.8 mm.	160-170°	Light red	0.8 g.
II	96-100°C.	2.8 mm.	170-180°	Light orange-red	2.2 g.
III	106-116°C.	2.4 mm.	180-185°	Light orange-red	17.0 g.

Yield - 17.0 g. or 81.0%

This fraction was redistilled with the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I	96-100°C.	1.0 mm.	185°	Light orange-red	1.5 g.
II	102-104°C.	1.0 mm.	185-188°	Light orange-red	13.0 g.

Yield - 13.0 g. or 61.9%

The boiling point of tetrahydroquinoline was 93-94°C. at 1.4 mm. bath temperature 157°, and that of the distilled product was 102-104°C. at 1.0 mm., bath temperature 185-188°. These boiling points were so close together that it was possible that the product might have been tetrahydroquinoline. However, the amount of low boiling fraction or the residue did not correspond to the weight of 2-nitrobutene-1 added and the weight of the pure product was greater than that of tetrahydroquinoline added.

The melting point of the tetrahydroquinoline hydrochloride is recorded as 180-181°C. It was easily prepared by warming

2.66 g. of tetrahydroquinoline with the theoretical amount of concentrated hydrochloric acid.

After recrystallizing from alcohol the needle-like white crystals melted at 179.5-181°C.

An attempt was made to prepare the hydrochloride of the product obtained by the reaction of 2-nitrobutene-1 with tetrahydroquinoline. To 2.34 g. of the compound was added the theoretical amount of concentrated hydrochloric acid (0.81 cc.). The solution turned dark green and an oil appeared on the surface. A slight odor of 2-nitrobutene-1 could be detected. The reaction mixture was placed on a steam-bath. The solution turned dark brown and the severe lacrimatory effect of the 2-nitrobutene-1 could be noted. In about ten to fifteen minutes after placing on the steam-bath, a thick, sticky mass formed which resembled a polymer of 2-nitrobutene-1. This can probably be explained on the basis that 1-tetrahydroquinoline-2-nitrobutane is not stable toward concentrated hydrochloric acid. It also appeared that the compound broke down to form the original reactants. The tetrahydroquinoline in acid medium must then catalyze the formation of the polymer. After standing for two months the polymer was quite hard. A very few fine, white crystals could be seen on the edge of the evaporating dish. There were so few of these crystals that they could not be extracted from the heavy residue. However, they resemble in appearance the hydrochloride of tetrahydroquinoline.

The hydrochloride is often more easily prepared by bubbling

dry gaseous hydrogen chloride through a solution of the compound in an organic solvent. Four tenths of a gram of the compound was dissolved in 10 cc. of dry benzene and dry hydrogen chloride was passed through. The solution darkened after a very few minutes utes and a dark residue resembling the polymer of 2-nitrobutene-1 formed on the bottom of the flask. The hydrogen chloride was passed through for over an hour, but the hydrochloride failed to form.

It can be seen from the fractional distillation that there was very little low boiling material and only a small amount of residue. This would indicate that the 2-nitrobutene-1 must be combined in some way with the tetrahydroquinoline since any unreacted 2-nitrobutene-1 would distill at a very low temperature or remain as a polymer in the distilling flask.

Since the theoretical percentages of nitrogen in tetrahydroquinoline and 1-tetrahydroquinolino-2-nitrobutane are 10.52 and 11.96 respectively, a nitrogen determination should distinguish between these. A nitrogen determination was correct for 1-tetrahydroquinolino-2-nitrobutane.

% N Found		% N Calculated	
11.71	11.46	1-tetrahydroquinolino-2-nitrobutane	11.96
		tetrahydroquinoline	10.52
		2-nitrobutene-1	13.84

The preparation of a crystalline derivative was found to be very difficult. The picrate was attempted, using several variations of the standard procedure, but the characteristic brown polymer resulted. An attempt to form the picrate by adding .3 g.

of the compound to 0.3 g. of picric acid and heating until melted proved unsuccessful and the polymer resulted.

Three more attempts were made to form the picrate using different methods. In the first test the standard procedure was used. The second test was made by adding 0.3 g. of the compound directly to the saturated picric acid and bringing it almost to the boiling point. In the third test, 0.3 g. of compound were added directly to 10 cc. of saturated picric acid solution and warmed. No crystals formed on cooling, but the latter two tests did not turn brown. After standing about two weeks, a few crystals were found in the second one. In three weeks quite a few large rectangular yellow crystals had formed in this test, and a very few had formed in the third. The crystals from the second test were filtered by suction and recrystallized from alcohol. The large rectangular crystals formed slowly upon cooling the alcohol solution.

The crystals were dried overnight in a desiccator. The finely ground crystals had a sharp melting point (135-136°C.), (136-137°C. corrected). The picrate turned red at 132-133°C., but did not start to melt until 135°C. It was entirely liquid at 136°C. A nitrogen determination gave the following results:

% N Found	% N Calculated
15.26 14.98	1-tetrahydroquinolino-2-nitrobutane picrate 15.11

6. Tetrahydroquinoline (Second Preparation)

To 0.15 mole (15.31 g.) of 2-nitrobutene-1 was added dropwise the theoretical amount (19.99 g.) of tetrahydroquinoline.

The reaction temperature rose very slowly until about 8.0 g. had been added. It then rose rapidly to 60°C. The rate of addition was controlled to maintain a 60°C. temperature. The viscous, light red oil was fractionally distilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	87°C.	2.4 mm.	170°	Red	1.5 g.
II	87-102°C.	2.4 mm.	170°	Light red	1.1 g.
III	102-108°C.	2.4 mm.	160-170°	Light red	28.7 g.

Yield - 28.7 g. or 81.3%

Fraction III was redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I	90°C.	2.3 mm.	150°	Light red	0.0 g.
II	90-102°C.	2.3 mm.	160°	Light red	0.6 g.
III	102-108°C.	2.6 mm.	156-160°	Light red	26.0 g.

Yield - 26.0 g. or 73.7%

A boiling point determination showed that the compound boiled at 106-108°C. (107-109°C. corrected), at 2.6 mm., bath temperature 156-160°C.

A nitrogen determination on Fraction III gave satisfactory results for 1-tetrahydroquinolino-2-nitrobutane.

% N Found		% N Calculated	
11.95	11.51	1-tetrahydroquinolino-2-nitrobutane	11.96
		tetrahydroquinoline	10.52
		2-nitrobutene-1	13.84

7. Reduction of 1-Tetrahydroquinolino-2-nitrobutane

Ten grams of 1-tetrahydroquinolino-2-nitrobutane were dissolved in 175 cc. of absolute alcohol and 10.0 g. of Raney nickel

were added. Hydrogenation was carried out in a Parra bomb hydrogenator. After thirty minutes at 40-lbs. pressure, only a very slight drop in pressure was noticed. The hydrogenation bottle was removed and heated on a steam-bath to the boiling point of the alcohol. Hydrogenation was continued at 50-lbs. pressure. In one hour the pressure was constant at 44 lbs. The bottle was removed and the Raney nickel filtered off and 10.0 g. of fresh Raney nickel added. Further hydrogenation of the hot solution did not consume any more hydrogen. The Raney nickel was filtered off and the alcohol removed by distillation. The reduced product distilled as follows:

Fraction	Temp.	Pressure	Bath	Color	Yield
I_1	102-105°C.	1.4 mm.	145-160°	Light yellow	1.3 g.
II_1	106-109°C.	1.0-1.5 mm.	160-168°	Light yellow	0.6 g.
III_1	145-149°C.	1.0-1.5 mm.	200-205°	Light yellow	3.5 g.

Considerable non-volatile material remained in the flask.

8. Reduction of 1-Tetrahydroquinolino-2-nitrobutane (Second Preparation)

Due to the small yield in the above, 12.0 g. of the compound were reduced as before. A drop of 11-lbs. pressure was noted. Distillation gave the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I_2	96-110°C.	1.5 mm.	179°	Light yellow	1.5 g.
II_2	110-120°C.	1.5 mm.	180°	Light yellow	2.5 g.
III_3	144-146°C.	1.5 mm.	180-200°	Light yellow	3.5 g.

Fractions III_1 and III_2 were combined and redistilled (5½ g.)

Fraction	Temp.	Pressure	Bath	Color	Yield
I$_3$	117-127°C.	1.0-1.5 mm.	205°	Light yellow	2.0 g.
II$_3$	127-140°C.	1.0-1.5 mm.	205°	Light yellow	
III$_3$	143-146°C.	1.0-1.5 mm.	210-230°	Light yellow	3.0 g.

The nitrogen content in Fraction III$_3$ was determined, using the Kjeldahl method for amines.

% N Found	% N Calculated
8.10 8.04	1-tetrahydroquinolino-2-amino butane 13.72

9. Reduction of 1-Tetrahydroquinolino-2-nitrobutane (Third Preparation)

The previous yields were very low and the nitrogen content implied that complete reduction had not taken place. A reduction using aluminum-amalgam was attempted, using 20.0 g. of the amalgam and 15.0 g. of the undistilled 1-tetrahydroquinolino-2-nitrobutane dissolved in 120 cc. of ether and 2 cc. of water. Hydrogen was liberated very rapidly. Reduction was carried out for four and a half hours. The aluminum-amalgam was filtered off and the ether removed by evaporation. The clear yellow liquid which remained was distilled under reduced pressure.

Fraction	Temp.	Pressure	Bath	Color	Yield
I$_4$	155°C.	5 mm.	215°	Reddish yellow	3.0 g.
II$_4$	156-160°C.	5 mm.	215°	Yellow	1.5 g.
III$_4$	160-175°C.	4 mm.	215-247°	Reddish yellow	5.0 g.

When the bath reached 180°C., white puffs of smoke indicated some decomposition.

10. Reduction of 1-Tetrahydroquinolino-2-nitrobutane (Fourth Preparation)

Since some decomposition occurred in the previous distillation, it was believed advisable to distill the reaction mixture before carrying out the reduction.

Fifteen grams of the distilled product were reduced with aluminum-amalgam in 200 cc. of ether and 1 cc. of water. After removing the aluminum-amalgam and ether, the compound was distilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I_5	102-110°C.	3.0 mm.	160-172°	Light yellow	2.2 g.
II_5	110-130°C.	3.0 mm.	172-200°	Light yellow	1.5 g.
III_5	139-169°C.	3.6 mm.	200-240°	Reddish yellow (slight decomposition)	2.5 g.

Combined Fractions II_4, III_4, II_5, and III_5 were redistilled (12 g.)

Fraction	Temp.	Pressure	Bath	Color	Yield
I	94-97°C.	2.0 mm.	144-146°	Light yellow	
II	100-102°C.	2.0 mm.	175°	Light yellow	
III	120-147°C.* 147-150°C.	2.0 mm.	175°	Light yellow	5.0 g.

*A very few drops distilled between 120-147°C.

A nitrogen determination was made on Fraction III, using the Kjeldahl method for amines.

% N Found	% N Calculated
8.23 8.11	1-tetrahydroquinilino-2-amino butane 13.72

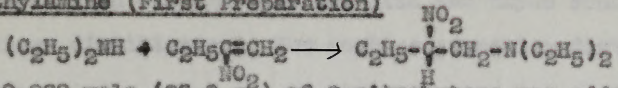
A nitrogen determination using the Kjeldahl procedure for nitro compounds gave the following results:

% N Found

12.41 12.51 12.61

From the above it can be seen that complete reduction has not yet been accomplished.

11. Diethylamine (First Preparation)



$$(C_2H_5)_2NH + C_2H_5\underset{NO_2}{C}{=}CH_2 \longrightarrow C_2H_5-\overset{NO_2}{\underset{H}{C}}-CH_2-N(C_2H_5)_2$$

To 0.228 mole (23.0 g.) of 2-nitrobutene was added 0.228 mole (16.8 g.) of diethylamine at such a rate as to maintain a temperature of 50-60°C. After only a few cubic centimeters had been added, a very violent reaction took place and the compound decomposed due to the heat of reaction.

12. Diethylamine (Second Preparation)

The second preparation was carried out using 0.114 mole of each reactant. The reaction was carried out in an ice-bath in order to maintain the temperature at 40°C.

The product distilled as follows:

Fraction	Temp.	Pressure	Bath	Yield
I_1	68°C.	24.0 mm.	105°	1.2 g.
II_1	68-69°C.	21.0 mm.	109°	2.2 g.
III_1	80-84°C.	19.0 mm.	145-157°	2.7 g.

This compound distilled with decomposition and a large amount of residue was left in the flask. The rate of decomposition prevented a lower pressure with the water aspirator.

13. Diethylamine (Third Preparation)

This reaction was carried out at 40°C. using 0.148 mole of each reactant. An attempt was made to carry out this distillation at a lower pressure in order to prevent decomposition, but the vacuum pump would not produce a pressure lower than 20 mm. because of the decomposition vapors. All of the volatile mater-

ial was distilled off and combined with the three fractions from the previous distillation. The combined fraction distilled as follows:

Fraction	Temp.	Pressure	Bath	Yield
I_2	60°C.	15-16 mm.	109°	1.4 g.
II_2	60-70°C.	15-16 mm.	115°	3.1 g.
III_2	70-78°C.	15-16 mm.	125°	5.2 g.

Fractions II_2 and III_2 were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Yield
I_3	64°C.	15 mm.	100°	0.9 g.
II_3	64-69°C.	15 mm.	105°	1.0 g.
III_3	69-75°C.	15 mm.	105-122°	1.5 g.

The above distillation did not yield a good quantity of a definite boiling compound, and therefore a nitrogen determination would be of little value.

14. Diethylamine (Fourth Preparation)

To 0.386 mole (39.0 g.) of 2-nitrobutene-1 was added 0.386 mole (28.0 g.) of diethylamine. The reaction was kept below 30°C. The resulting compound was an orange-red oil which distilled as follows:

Fraction	Temp.	Pressure	Bath	Yield
I_4	54°C.	32 mm.	99°	0.95 g.
II_4	54-70°C.	47 mm.	100°	2.0 g.
III_4	70-77°C.	47-17 mm.	100°	15.2 g.
IV_4	77-90°C.	18 mm.	100-159°	

When the bath reached 95-100°C., an apparent exothermic re-

action started in the flask. The distillation started more rapidly and the pressure rose from 32 to 47 mm. The bath was lowered but the reaction and distillation continued for some time. When the reaction had subsided, the oil bath was replaced. The pressure gradually lowered to 18 mm. Fraction IV distilled with puffs of smoke. A large residue resembling the 2-nitrobutene-1 polymer remained in the flask.

A refractionation of the above distillate gave the following results:

Fraction	Temp.	Pressure	Bath	Yield
I_5	room	15-16 mm.	room	1.7 g.
II_5	70°C.	13 mm.	124°	1.9 g.
III_5	70-81°C.	13 mm.	124°	9.2 g.
IV_5	81-110°C.	13-15 mm.	225°	2.4 g.

The fractions boiling from 70-80° were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Yield
I_6	66°C.	15-16 mm.	100°	1.1 g.
II_6	66-70°C.	16 mm.	112°	4.4 g.
III_6	70-77°C.	16 mm.	118°	7.2 g.

Fractions II_6 and III_6 were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Yield
I_7	67°C.	16-17 mm.	107°	0.9 g.
II_7	67-69°C.	16-17 mm.	107°	2.5 g.
III_7	69-71°C.	16-17 mm.	107°	6.0 g.

Since Fraction III_7 had a fairly close boiling range, a nitrogen determination was made. The nitrogen content was too

low for the predicted product.

% N Found	% N Calculated	
12.73 13.23 12.70	Diethylamino-2-nitrobutane	16.08
	2-nitrobutene-1	13.84
	Diethylamine	19.27

15. Diethylamine (Fifth Preparation)

Another attempt was made to prepare this compound by carrying out the reaction at 0°C., using 0.252 mole (18.4 g.) of diethylamine and 0.252 mole (25.5 g.) of 2-nitrobutene-1.

The reaction mixture distilled as follows:

Fraction	Temp.	Pressure	Bath	Yield
I_8	62°C.	19 mm.	112°	2.5 g.
II_8	62-79°C.	20 mm.	116°	4.0 g.
III_8	79-81°C.	19-20 mm.	113°	5.7 g.
IV_8	80-85°C.	8 mm.	113°	5.6 g.

The percentage of nitrogen was determined in Fractions II_8 and III_8. The determination was not correct for 1-diethylamino-2-nitrobutane.

% N Found - Fraction II_8	% N Calculated	
13.57 13.74	diethylamino-2-nitrobutane	16.08

% N Found - Fraction III_8	% N Calculated	
13.61 13.67	diethylamino-2-nitrobutane	16.08

Fractions IV_8 and I_8 were distilled as follows:

Fraction	Temp.	Pressure	Bath	Yield
I_9	60°C.	5 mm.	100°	2.0 g.
II_9	60-68°C.	5 mm.	100-120°	3.5 g.

Fraction II_8, II_9, and III_8 were combined and fractionated.

Fraction	Temp.	Pressure	Bath	Yield
I_{10}	60°C.	5 mm.	105°	2.0 g.
II_{10}	62-67°C.	5 mm.	100-110°	8.0 g.

A nitrogen determination on II_{10} was not correct for the desired product.

% N Found	% N Calculated	
12.41 13.05	1-diethylamino-2-nitrobutane	16.08

Since the amine compounds usually boil somewhat lower and are often more stable than the corresponding nitro compounds, it was believed that the reduced compound might be isolated. About 8.0 g. of the nitro compound were dissolved in 60 cc. of ether and reduced for four and a half hours with 10.0 g. of aluminum-amalgam. When the ether had been removed, about 4-5 g. of a light yellow liquid with an amine odor remained.

To a small portion of the amine dissolved in benzene was added benzoyl chloride. Heat was liberated but no crystals could be obtained. To another small portion of the reduced compound dissolved in benzene were added benzoyl chloride and a few drops of dilute hydrochloric acid. After four days, long, white crystals appeared surrounded by a black gum. These crystals have not yet been identified.

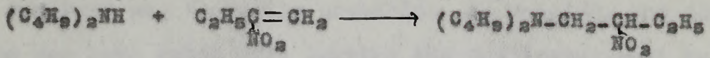
In spite of the repeated distillations, an attempt to isolate the desired product failed. No definite boiling fraction could be obtained after the several preparations and the nitrogen content was low for the desired product.

The results of this work indicated that polymerization,

rather than addition, had taken place. The formation of varying amounts of the dimer and trimer in the several preparations would explain the failure to obtain a definite boiling fraction. Further evidence for polymerization has been shown by the percentage of nitrogen found in the Fractions III_7, II_8, III_8, and II_{10}. Although these fractions boil at different temperatures, the nitrogen value is approximately the same and corresponds very closely to that of 2-nitrobutene-1.

In no case was the diethylamine recovered quantitatively from this reaction mixture, but the behavior on distilling was very similar to that when pyridine was used as a catalyst for polymerization.

16. Di-n-butylamine (First Preparation)



$$(C_4H_9)_2NH + C_2H_5\underset{NO_2}{C}{=}CH_2 \longrightarrow (C_4H_9)_2N\text{-}CH_2\text{-}\underset{NO_2}{CH}\text{-}C_2H_5$$

The reaction between di-n-butylamine and 2-nitrobutene-1 was carried out at 30°C. by adding 0.148 mole (19.2 g.) of di-n-butylamine dropwise to 0.148 mole (15.0 g.) of 2-nitrobutene-1. The reaction was very exothermic and resulted in an orange liquid. The compound distilled as follows:

Fraction	Temp.	Pressure	Bath	Color	Yield
I	57°C.	19 mm.	113°	Yellow	2.2 g.
II	57-66°C.	20 mm.	114°	Yellow	3.47 g.
III	66-71°C.	20 mm.	113-119°	Reddish yellow	10.0 g.
IV	100-112°C.	19 mm.	160-180°	Reddish	8.0 g.

This reaction mixture behaved like the diethylamine upon distilling. The reaction mixture turned dark and it appeared as though a reaction were taking place. A very hard black residue remained in the flask.

Fractions II and III were redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I_2	50°C.	15.5 mm.	87°	Yellow	2.1 g.
II_2	50-55°C.	15.5 mm.	89°	Clear	4.0 g.
III_2	55-57°C.	15.5 mm.	90°	Clear	5.1 g.

The above distillation took place very slowly. It appeared that the compound was thermally unstable. On heating, the dibutylamine may have split off, leaving the 2-nitrobutene-1 to polymerize in the flask. The boiling point, odor, and color of the above fractions indicated that the distillate was dibutylamine.

Fraction IV contained a considerable quantity of compound. It was fractionated as follows:

Fraction	Temp.	Pressure	Bath	Color	Yield
I$_3$	70°C.	15.5 mm.	150°	Light yellow	0.5 g.
II$_3$	97°C.	15.5 mm.	155°	Yellow	3.0 g.
III$_3$	95-97°C.	15.5 mm.	145-160°	Yellow	3.5 g.

Fractions II$_3$ and III$_3$ were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I$_4$	70°C.	15.0 mm.	130°	Yellow	Few drops
II$_4$	94°C.	15.0 mm.	150°	Yellow	Few drops
III$_4$	96-98°C.	15.0 mm.	145-150°	Reddish	1.5 g.
IV$_4$	98-112°C.	15.0 mm.	150-180°	Yellow	2.5 g.

In all of the above distillations no definite compound was obtained. The first conclusion was that the compound was distilling from the residue and thus no definite boiling point could be obtained. However, on redistillation no sharp fractions could be obtained and the compound seemed to be breaking up, yielding some dibutylamine and a residue.

17. Di-n-butylamine (Second Preparation)

The addition of dibutylamine was attempted by mixing 0.148 mole of the reactants at 0°C. A cherry red, viscous liquid resulted, and fractionation gave the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I_5	55°C.	3.0 mm.	107°	Light yellow	0.9 g.
II_5	55-75°C.	3.0 mm.	110°	Yellow	1.7 g.
III_5	73-76°C.	3.0-5.0 mm.	110-112°	Red	18.0 g.

In the above distillation a fair yield of compound boiling at 73-76° was obtained. It was possible to maintain a pressure from 3-5 mm., and very little decomposition was noted. It appeared as though the lower temperature had aided the addition and prohibited extensive polymerization.

Fractions II_5 and II_3 were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I_6	45°C.	2.0 mm.	95°	Yellow	9.5 g.
II_6	65°C.	2.0 mm.	112°	Yellow	Few drops
III_6	70-78°C.	2.0 mm.	110-115°	Yellow	5.0 g.

In the above distillation the oil bath was inadvertently heated to 90°C. before the pressure was reduced. After cooling the bath, the pressure was reduced and the compound distilled as indicated. The large portion of yellow liquid distilling in Fraction I_6 corresponded to dibutylamine and indicated that addition must have taken place, and that the compound is thermally unstable.

A nitrogen determination on Fraction III_6 was not successful.

% N Found	% N Calculated
11.53 11.61	1-dibutylamino-2-nitrobutane 12.49

18. Di-n-butylamine (Third Preparation)

The compound was prepared again as in the second preparation. Fractionation gave the following results:

Fraction	Temp.	Pressure	Bath	Color	Yield
I_7	60°C.	3.5 mm.	111-112°	Red	8.0 g.
II_7	60-71°C.	3.0 mm.	114°	Reddish yellow	2.0 g.
III_7	71-76°C.	3.0-5.0 mm.	114-119°	Light red	18.0 g.

The distillation of Fraction III_7 was very slow. The entire distillation required one and a half to two hours. There was a considerable amount of residue left and some of the dibutylamine was found in the trap.

Fractions II and III were combined and redistilled.

Fraction	Temp.	Pressure	Bath	Color	Yield
I_8	69°C.	3.0 mm.	114°	Yellow	5.0 g.
II_8	74-77°C.	3.0 mm.	117°	Reddish	2.0 g.
III_8	76-78°C.	3.0 mm.	117-120°	Red	7.0 g.

A nitrogen determination on Fraction III_8 gave the following results:

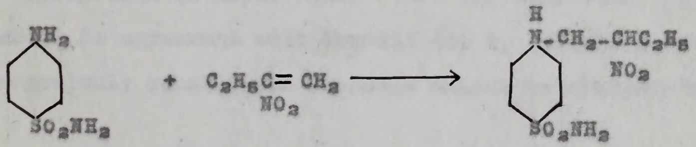
% N Found		% N Calculated	
11.19	11.37	1-dibutylamino-2-nitrobutane	12.49

The above attempts failed to yield a pure addition product with di-n-butylamine. However, there was considerable evidence indicating that this reaction had occurred. The high heat of reaction suggested either addition or polymerization. The first fractionation indicated that both reactions may have taken place. In no instance was the di-n-butylamine quantitatively removed on distilling as was the case when pyridine was used on

page 33. By lowering the temperature, an increased amount of the higher boiling fraction could be obtained. After repeated distillations of this fraction, a large portion of low boiling material corresponding to the di-n-butyl amine was obtained. This indicated that the di-n-butyl amine must have been added, but the compound was thermally unstable, splitting off the di-n-butylamine and leaving a polymer of 2-nitrobutene-1 in the distilling flask.

Although a pure compound was not isolated, it should be noted that a decrease in temperature caused an increase in the quantity of the high boiling fraction. Since Cerf de Mauny found that nitro compounds distilled under nitrogen with much less decomposition, it is possible that the decomposition could have been prevented in this way. In view of the above work, it is believed that if this reaction could be carried out at a lower temperature and fractionally distilled under nitrogen, the desired product could be isolated.

19. p-Aminobenzenesulfonamide



About 0.05 mole (5.05 g.) of freshly prepared 2-nitrobutene-1 was added to 0.05 mole (8.61 g.) of p-aminobenzenesulfonamide.[1]

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[1] Prepared according to Adams and Johnson (1).

The nitrobutene was absorbed but no temperature change could be detected. The reaction mixture was dissolved in 20 cc. of acetone by heating to 50°C. on a steam-bath. The resulting solution had an orange-red color but no evidence of reaction was noticed. The sharp odor of 2-nitrobutene-1 was very apparent. The mixture was again heated to 50°C. and allowed to cool. The lacrimatory effect was decreased but the deep red color indicated some polymerization. No crystals formed on standing in the ice-chest overnight.

About one-half of the acetone solution was placed in an eight-inch test tube and refluxed for about forty minutes. The solution turned dark red and the odor of 2-nitrobutene-1 was removed. The test tube was placed in the ice box for about three hours but no crystals formed. The mixture was placed on a watch glass and the acetone allowed to evaporate. After several days a very dark, brown-red, sticky mass was formed. It was concluded that the addition had not been effected.

This reaction is theoretically possible and it is believed that an appropriate catalyst would cause the addition. However, this work is in agreement with Worrall (3, 6, 10) who was unable to add negatively substituted aromatic amines to nitrostyrene.

III. SUMMARY

The polymerization of 2-nitrobutene-1 has been carried out by the use of several different catalysts. Polymers have been formed ranging in composition from light oils to solids, depending on: the catalyst chosen, the temperature, and the time for formation.

The most effective catalysts found were organic and inorganic bases. Some amines such as dicyclohexylamine caused a violent polymerization, leaving a viscous liquid which later formed a solid. Pyridine, when used at about 0.1% concentration, has been shown to cause a rather slow polymerization forming a viscous liquid. Sodium hydroxide formed polymers varying from viscous liquids to taffy-like solids, depending on the concentration and the temperature. At higher temperatures, the polymers were formed much faster and were somewhat more dense in the case of sodium hydroxide. An increase in the concentration of sodium hydroxide caused an increase in density and hardness. However, with amines, high temperatures or an excessive amount of catalyst cause explosive polymerization.

Of the above polymers the viscous liquid formed when pyridine was used as a catalyst, and the solid formed by 10% sodium hydroxide, were chosen for further study. The former was reduced to the corresponding amine over Raney nickel, but little was found concerning its exact structure. The original liquid

polymer was found to be soluble in sodium hydroxide and reprecipitated by acid. If the predicted structure is correct, solubility must be caused by a secondary nitro group on the end of the linear polymer. The reduced compound was soluble in hydrochloric acid but was not dissolved by sodium hydroxide.

The preparation of N-nitroalkylamines by the addition of amines to 2-nitrobutene-1 has also been studied. This reaction has been carried out with the following secondary amines:

Amine Used	Boiling Point	Yield*	Nitrogen %Calc.		Nitrogen %Found
Morpholine	137-139°C. 15 mm.	84.8% 78.8%	14.69	14.78	14.89
Piperidine	118-121°C. 14 mm.	84.1% 80.1%	16.42	16.15	16.54
Tetrahydroquinoline	107-109°C. 2.6 mm.	81.3% 73.7%	11.95	11.51	11.96
Diethylamine	- not isolated				
Dibutylamine	- not isolated				
p-Aminobenzenesulfonamide	- not isolated				

*The first yield was taken after one fractionation and the second after two fractionations.

Derivatives		Nitrogen % Found		% Calc.
1-Morpholino-2-Nitrobutane Picrate	137-138°C.	16.48	16.52	16.54
1-Piperidino-2-Nitrobutane Picrate	125-126°C.	16.69	16.40	16.79
1-Tetrahydraquinolino-2-nitrobutane Picrate	136-137°C.	15.20	14.98	15.11

The attempt to add p-aminobenzenesulfonamide to 2-nitro-

butene-1 failed. This coincides with Worrall's findings (63) that this reaction under these experimental conditions is limited due to the ease of polymerization of the 2-nitrobutene-1, and because substituents in the ring of aromatic derivatives have a hindering effect. However, the former difficulty should be eliminated by the use of a nitroölefine which does not contain the group $C{=}CH_2$, and the latter condition cannot be applied too generally since Mason and Gitchel were able to add p-nitroaniline to 2-nitrobutene-1.

The N-nitroalkylamines which were isolated were prepared from heterocyclic amines. Although the isolation of a pure compound was not obtained in the case of a secondary aliphatic amine, there is considerable evidence that the addition was accomplished.

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